tailor them for specific uses. In general these materials have found use as catalysts, ion exchangers and adsorbents and are also useful in gas and liquid separation processes (where they exhibit molecular sieving properties similar to those of zeolites). Some examples are:

1. Organoclays containing molecules such as $(CH_3)_4N^+$ are especially suited for certain separation processes due to their hydrophobic nature and high affinity for certain organic compounds.
2. Clays and their oxide-pillared derivatives have found use as: (i) scavengers for hazardous organics (especially from effluent streams); (ii) selective adsorbents of heavy metals from effluent streams; and (iii) purifiers for edible oils where the clays adsorb compounds such as carotenoids and chlorophyll to give the oil its clear look and taste. Indeed acid activated clays are the industry standard for the decolorizing of oil.
3. LDHs have found use as excellent acid residue scavengers.

Greater use of layered materials in separation processes can be achieved when the materials are used in the form of membranes where they act as ionic and molecular filters or sieves.

See also: **II/Ion Exchange:** Historical Development; Novel Layered Materials: Phosphates; Organic Ion Exchangers; Organic Membranes.

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Organic Ion Exchangers

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Abstract

The definition and some characteristic concepts regarding organic ion exchangers are pointed out. The development of these ion exchangers, beginning with chemically modified natural products and continuing with the synthetic ones, is further presented. A classification of organic ion exchangers is proposed according to several criteria, such as the synthesis method, morphology of the three-dimensional network, their physical shape and the nature of their functional groups.

Of the general characteristics of organic ion exchangers only the exchange capacity and selectivity are briefly discussed.

Preparation and structure – chemical property relationships, and some applications with reference to strong and weak cation and anion exchangers, as well as to chelating ion exchangers – are described in more depth.

Definition

An ion exchanger generally is a solid, insoluble material that contains groups which ionize in aqueous medium.

Organic ion exchangers are three-dimensional covalent networks that contain exchangeable ions associated with fixed acid or basic groups. The term 'ion exchange resins' is also used to describe organic ion exchangers.

The ion exchangers that have fixed acid groups and carry exchangeable cations (usually H^+ or Na^+) are cation exchangers described as in the H form and Na

form, respectively. Those with fixed base groups and exchangeable anions (OH^- or Cl^-) are anion exchangers in the OH form and Cl form, respectively.

In the accepted terminology, the three-dimensional network with the fixed groups is called the matrix or framework and exchangeable ions of opposite sign, which neutralize the fixed ionic groups, are the counter-ions that are responsible for the ion exchange process.

Co-ions are mobile ions having the same sign as the fixed charges of the matrix. In fact, organic ion exchangers are crosslinked polyelectrolytes. Thus, a cation exchanger is an anionic polyelectrolyte while an anion exchanger can be regarded as a cationic polyelectrolyte.

General Aspects

The first organic ion exchanger that found technical application was a chemically modified natural product, namely a sulfonated coal, described in many patents during the 1930s.

Other exchangers were synthesized by sulfonation or phosphorylation of wood, paper, cotton, lignin and tannins, as well as by the crosslinking of pectins with formaldehyde or epichlorhydrin.

In 1935 the discovery by Adams and Holmes of ion exchange properties in the product of a reaction between phenol, or *m*-phenylenediamine, with formaldehyde started the development of synthetic organic ion exchangers. These products have a greater importance than those from a natural organic source and have found much wider technical application because of their greater chemical stability and mechanical strength as well as their very different physical and chemical structures.

Synthetic organic ion exchangers are obtained by the two principal reactions used to produce polymeric materials, namely polycondensation or addition polymerization of a mixture of co-monomers. In polycondensation, incorporation of a trifunctional co-monomer is required while in polymerization the presence of a bifunctional co-monomer is sufficient.

Most commercially available ion exchangers are from polymerization processes which create structures with higher hydrolytic and oxidative stabilities as well as better defined physical features and crosslinkings.

In the case of the polycondensation exchangers, the reaction between a co-monomer that carries base or acid groups and a crosslinking agent (formaldehyde, epichlorohydrine, etc.) is used.

In 1944, D'Alelio found that sulfonated styrene–divinylbenzene copolymers have ion exchange properties. This finding was the beginning of the polymerization ion exchangers.

These structures are made by the polymerization of a mixture of a monovinylic monomer with a basic or acidic group and a divinylic monomer. The achievement of a neutral network, called the precursor or starting material, followed by the introduction of basic or acidic groups by suitable polymer-analogous reactions, is often preferred.

Usually divinylbenzene (DVB) is used as the divinylic monomer and the quantity added, in terms of the percentage in the mixture of co-monomers, defines the degree of crosslinking of the network, although crosslinking side reactions can occur during the polymer-analogous transformations.

The structures created are called 'conventional' or 'gel'-type ion exchangers and generally have about 8% DVB for crosslinking. This amount is required to achieve a network with both mechanical strength and easy diffusion of exchangeable ions as the exchanger comes into contact with an aqueous phase when swelling of the network occurs.

Meitzner and Oline found that the copolymerization of styrene with DVB in the presence of an appropriate inert compound, called 'diluent' or 'porogene agent', gave a network with significant and measurable physical porosity in the dried state, generally containing internal pores having diameters larger than 3×10^{-9} m. This discovery led to significant progress in the field of synthetic ion exchangers, namely the development of macroporous resins. These exchangers offer the advantage that they can be used with non-aqueous solvents and have much higher sorption rates of ions and non-electrolytes than the conventional gel exchangers.

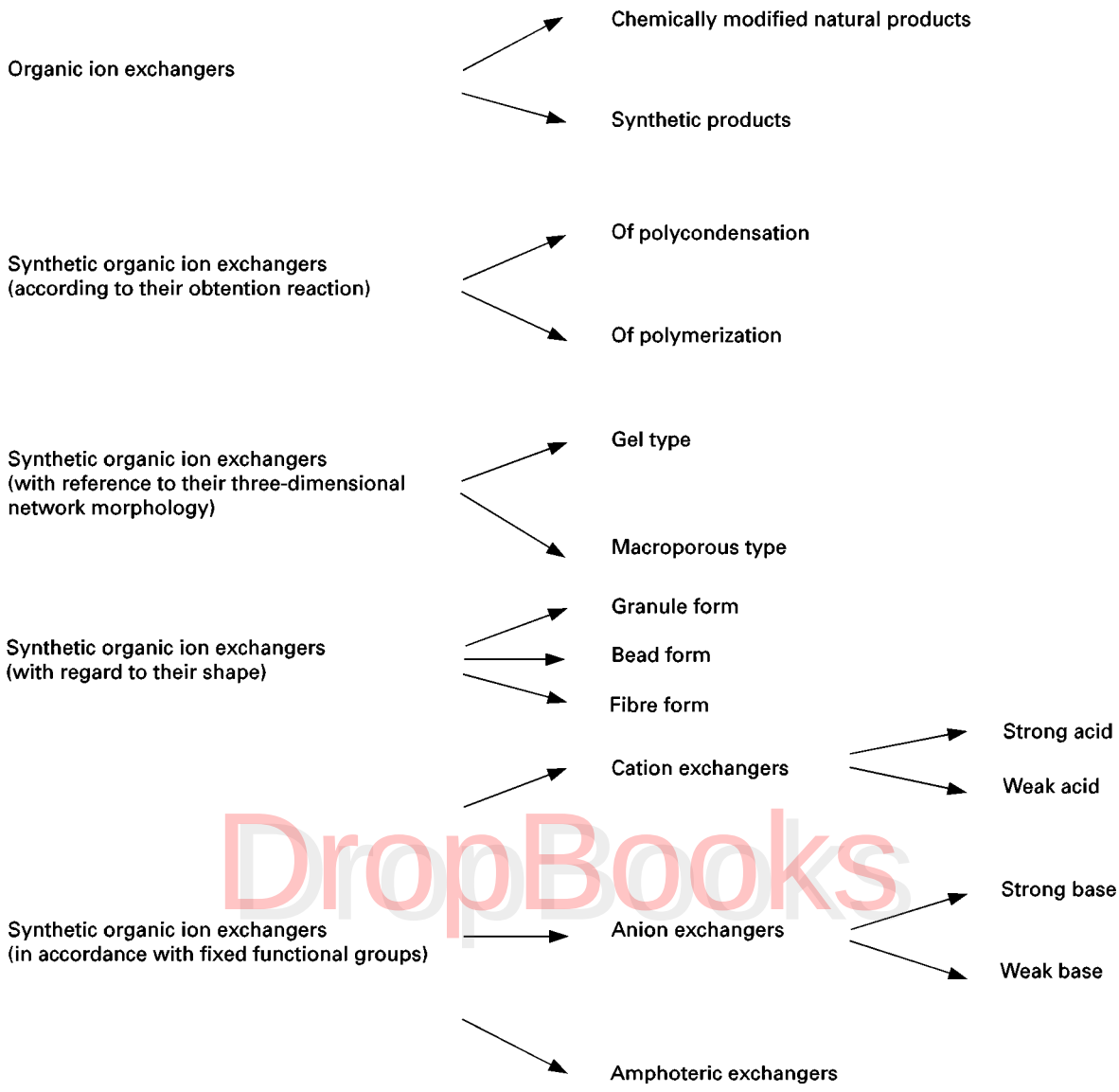
Polymerization produces exchangers in bead form, with a relatively wide distribution of size, by the suspension polymerization technique. More recently ion exchangers with uniform and controlled bead size have become available.

The polycondensation exchangers often appear as irregular-shaped particles, because they are made by bulk polycondensation followed by grinding of the bulk polymer into smaller particles. However, polycondensation exchangers can also be made in bead form by reverse-phase suspension polycondensation.

Ion exchangers in fibre form are also known, made by chemical modification of natural and synthetic fibres. Ion exchanger fibres have an improved kinetic performance when compared with the same structures in bead form.

Classification

Scheme 1 is a summary of the classification of organic ion exchangers. **Table 1** shows the most used



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Scheme 1 Classification of organic ion exchangers.

acid and base functional groups on organic ion exchangers.

Characterization

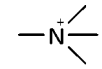
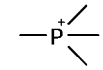
Ion exchange capacity is the most appropriate characteristic of organic ion exchangers.

The total capacity indicates the number of fixed acidic or basic groups per specified amount of ion exchanger. It can be described as both weight capacity and volume capacity, having as units milliequivalents per gram of dry exchanger (meq g^{-1}) and milliequivalents per cubic centimetre of fully swollen exchanger (meq cm^{-3}), respectively. If not otherwise stated, the capacity should be reported per gram of H form for a cation exchanger or the Cl form for an anion exchanger in the dry state. This capacity is a constant for the material and does not depend on the experimental conditions.

The effective capacity is the number of exchangeable counter-ions per specified amount of exchanger (the same units are used as above). This capacity depends on the experimental conditions and is lower than total capacity.

Another important characteristic is the selectivity which has a major role in the ion exchange processes. The selectivity is the preference of an ion exchanger for a particular counter-ion over the others, when it is

Table 1 Types of ion exchangers and their functional groups

Type	*Name of fixed functional group*	*Chemical structure of functional group*
Cation exchangers		
Strong acid	Aryl sulfonic	$-C_6H_5-SO_3H$
Weak acid	Carboxylic acid	$-COOH$
	Phenolic hydroxyl	$-C_6H_5-OH$
Intermediate acid	Phosphonic	$-P(O)(OH)_2$
	Phosphonous	$-P(O)H(OH)$
	Phosphoric	$-O-P(O)(OH)_2$
Anion exchangers		
Strong base	Quaternary ammonium	
	Phosphonium	
	Sulfonium	
Weak base	Primary amine	$-NH_2$
	Secondary amine	$-NHR$
	Tertiary amine	$-NR_2$
Amphoteric exchangers	Mixture of acid and base groups	

in contact with an electrolyte solution. The selectivity has various physical causes.

An ion exchanger tends to prefer a counter-ion with higher valence, lower solvatation, higher polarizability, stronger interactions with the fixed groups or the matrix, and less participation in complex formation with the co-ions. The selectivity of an ion exchanger is improved by increasing degree of crosslinking and by decreasing solution concentration and temperature.

Types of Synthetic Organic Ion Exchangers

Strong Acid Cation Exchangers

The most important strong acid cation exchangers are those of arylsulfonic acid type.

Polycondensation structures of this type can be obtained as follows:

1. By the sulfonation of a phenol followed by the condensation of the sulfonated product with formaldehyde.
2. By the sulfonation of a preformed phenol–formaldehyde three-dimensional network.

In the first method, the addition of unsulfonated phenol to provide the trifunctionality is essential. The structures created are illustrated in **Figure 1**.

A method for the synthesis of sulfonated condensation exchangers in bead form has been developed using organic solvents as dispersion media. This is an alternative to the grinding of bulk polymers as previously mentioned.

Most commercially available strong acid cation exchangers are those based on styrene–DVB copolymers with different morphologies of their three-dimensional networks. These products have higher capacities and better durabilities than their polycondensation predecessors. The common method for the production of these structures consists in sulfonation of the styrene–DVB copolymers with sulfonation agents such as sulfuric acid, sulfur trioxide, oleum or chlorosulfonic acid.

From the point of view of the mechanism, the sulfonation is an electrophilic substitution into an aromatic ring whereby the $-SO_3H$ group is attached in the *para*-position and a double sulfonation is probably impossible because of steric hindrance due to the polymer chain.

During the sulfonation reactions, crosslinking side reactions take place independent of the sulfonating agent, however chlorosulfonic acid apparently leads to the most crosslinks.

Side crosslinks are due to the inter-chain sulfone bridges that appear by reaction between the already attached $-SO_3H$ groups and the unreacted aromatic rings. Intra-chain sulfone bridges also can appear. The chemical structure of a sulfonated styrene–DVB copolymer is illustrated in **Figure 2**.

The pre-swelling with organic solvents of the copolymer beads before sulfonation reduces the number of sulfone bridges.

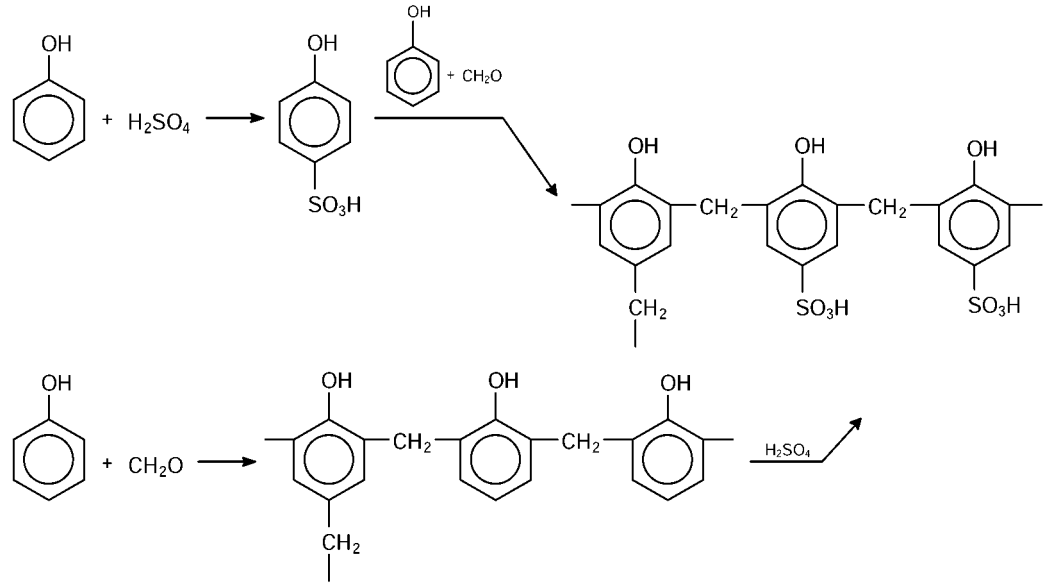


Figure 1 Preparation of sulfonated phenol–formaldehyde cation exchangers.

Addition to the styrene–DVB mixture of small amounts of a polar monomer, such as acrylonitrile, vinylpyridine, etc., improves the physical properties of the resultant ion exchanger – especially its resistance to osmotic shock because of the more uniform sulfonation reaction.

Sulfonations with the agents previously mentioned show some differences. Thus, reaction with sulfuric acid used the acid itself as a reaction medium hence a considerable excess of reagent is required. Reactions with chlorosulfonic acid or sulfur trioxide may be performed in an organic solvent, thus they need only a small excess of reagent over the stoichiometric quantities.

Sulfonations with the latter reagents take place at lower temperatures than with sulfuric acid which requires a temperature at about 100°C.

Post-sulfonation treatment of the sulfonated products is important to maintain whole beads. This can be achieved by the prevention of the changes that determine swelling, called 'osmotic shock', which leads to the disintegration of the beads. The gradual addition of water, or aqueous electrolyte solutions, decreases this deleterious effect.

Macroporous copolymer beads, because of their large internal surface areas, have a higher reactivity towards the sulfonation agents. They also require much lower quantities of organic swelling solvent, and are less susceptible to degradation by osmotic shock, both during preparation and in subsequent usage. In addition, they have a higher oxidation stability than the sulfonated structures of the gel type.

Strong acid cation gel-type exchangers have received major attention because of their utility in

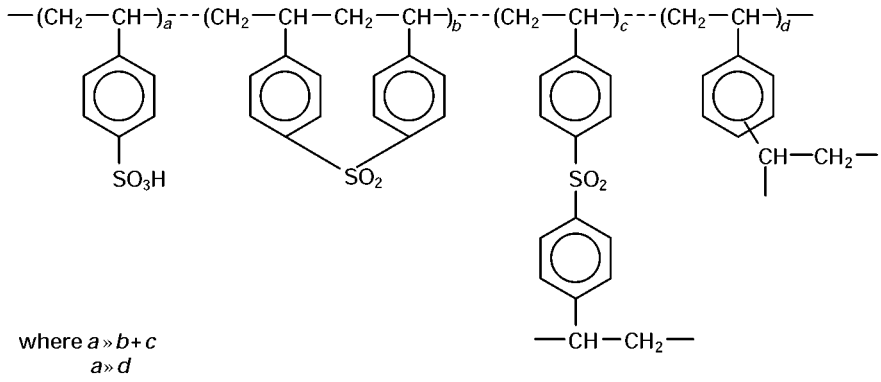


Figure 2 Chemical structure of sulfonated styrene–DVB copolymer-based cation exchanger.

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water softening which is their principal use. The equivalent macroporous structures can also be used as catalysts for certain reactions, particularly in non-aqueous media, instead of sulfuric and toluene-4-sulfonic acids. The resin catalysts show some advantages compared to low molecular weight acids, such as in their regeneration and potential reuse.

Because of their very high acidity, the aryl–SO_3H groups are fully ionized throughout the pH domain of aqueous solutions. The very low preference of the sulfonic-type cation exchanger for the H ion requires the use of large quantities of mineral acids for its regeneration to the H form after the exhaustion cycle, especially in water treatment processes.

The strong acid exchanger in its H form participates in ion exchange reactions with bases like NaOH and with alkaline or neutral salts. The latter reaction is called 'salt-splitting'.

Weak Acid Cation Exchangers

The polycondensation exchangers can be prepared by the reaction of salicylic acid, or 1,3,5-resorcylic acid, with formaldehyde. In the former case, the addition of phenol is required because one *ortho*-position is not accessible to the aldehyde.

Several polymerization networks that contain –COOH groups are known. Some structures together with their preparative routes are illustrated in **Figure 3**. Only those with acrylic networks are commercially available.

Compared with the sulfonic group the –COOH group, has a much lower acidity and is fully ionized only in an alkaline medium as a salt form. The –COOH group also shows a very considerable preference for the H ion, unlike the $-SO_3H$ group. This situation leads to easy regeneration of the weak acid exchangers from salt form to H form using stoichiometric quantities of mineral acids. These exchangers can react only with bases, like NaOH, and alkaline salts; they show a strong preference for Ca and Mg cations. The 'salt-splitting' reactions do not take place in the case of the weak acid cation exchangers.

The acrylic-type exchangers have a higher acidity than the methacrylic ones and can be used for the treatment of hard water containing large quantities of bicarbonates. The methacrylic type is used for special applications, such as the purification of antibiotics, where a mild pH is required.

Strong Base Anion Exchangers

Strong base anion exchangers are known only as polymerization products. Those with quaternary ammonium groups are the most common commercially available exchangers. Their preparation is performed by the chloromethylation of gel- or macroporous-type styrene–DVB copolymers in bead form, followed by the amination of the chloromethylated copolymers with trimethylamine or dimethylethanolamine leading to the so-called strong base anion exchangers of Types I and II, respectively. Their chemical structures are shown in **Figure 4**.

Usually the chloromethylation is carried out with monochloromethyl ether, in the presence of a Lewis acid ($ZnCl_2$, $AlCl_3$, $SnCl_4$, etc.) as catalyst. The reaction takes place under mild conditions: temperature about 50°C and reaction times of 5–8 h. Generally, the $-CH_2Cl$ groups are attached to over 90% of the *para*-positions of the styrene aromatic rings, following the chloromethylation of the mono alkylbenzene derivatives.

The main chloromethylation reaction is usually accompanied by a side alkylation reaction between pre-attached $-CH_2Cl$ groups and non-functionalized aromatic rings. Such a side reaction determines interchain and/or intra-chain methylene bridges that decrease the amount of $-CH_2Cl$ groups as well as the swelling capacity of the chloromethylated product. The latter aspect is especially prevalent in the case of gel-type copolymers. In most cases, the styrene–DVB macroporous networks show a reduction of their specific area and of the volume of their pores after chloromethylation, but an increase of the average diameter of the pores can be observed.

The use of a large excess of chloromethyl methyl ether or mixtures of chloroform or carbon tetrachloride with the halogenated ether reduces the side reaction.

An alternative route to obtain the chloromethylated styrene–DVB network is via the free-radical polymerization of chloromethylstyrene (vinylbenzyl chloride) with divinylbenzene. The first monomer is a 60 : 40 mixture of *meta*- : *para*-isomers.

The chemical structures of the two crosslinked polystyrene-based chloromethylated compounds or products are illustrated in **Figures 5A** and **B**. From these two figures one can see that the chloromethylstyrene–DVB copolymer (Figure 5A) has a more homogeneous chemical structure than the chloromethylated styrene–DVB copolymer (Figure 5B), but the former structure has the drawback of a much higher cost. For this reason chloromethylated styrene–DVB copolymers are chosen as the precursors to polystyrene-based anion exchangers.

Aminations of the chloromethylated styrene–DVB copolymers with trimethylamine and dimethylethanolamine take place easily, because the benzylic chlorine structure has a very high reactivity towards these nucleophilic reagents. Amination is performed

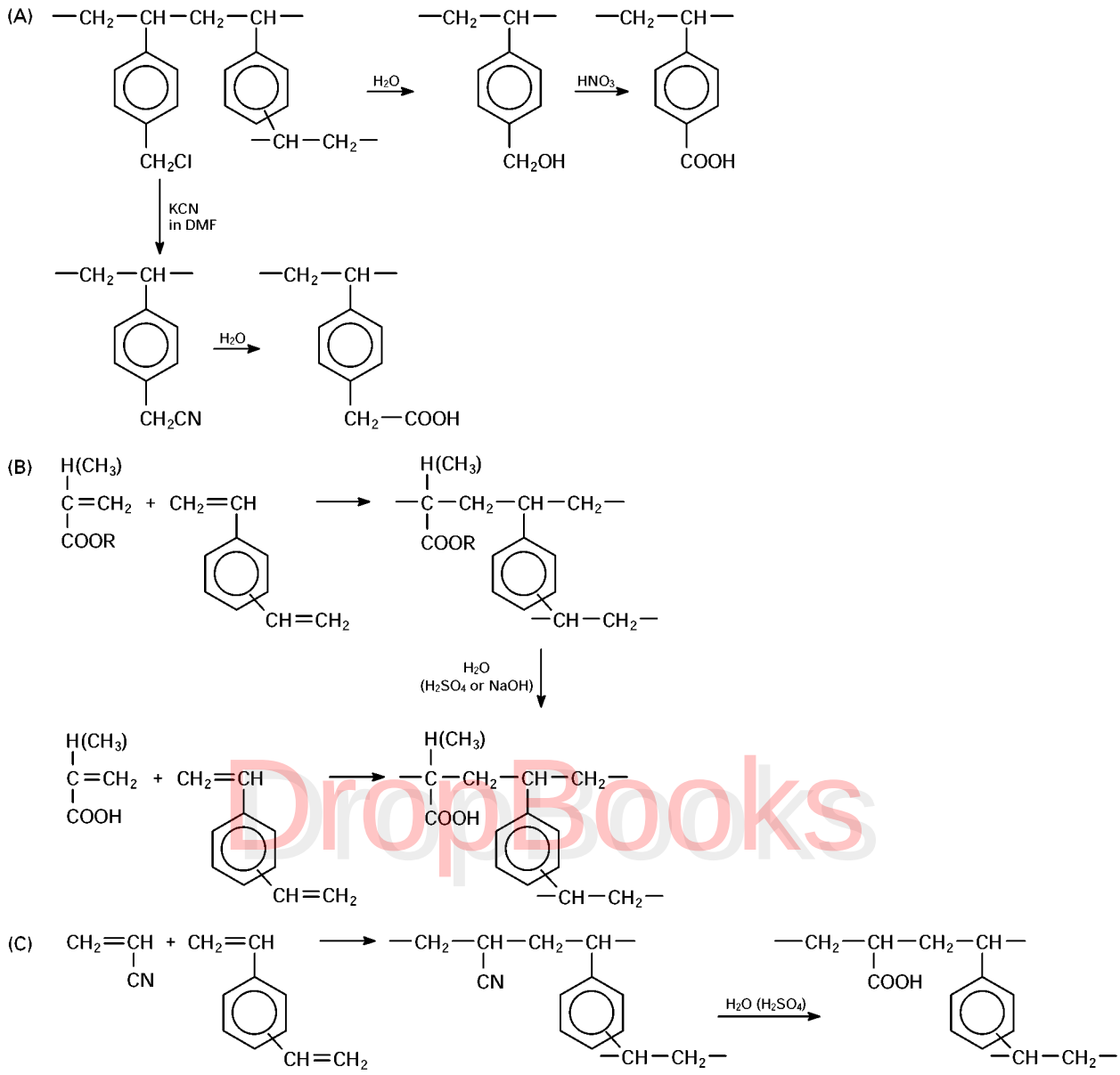

Figure 3 Some methods for the preparation of weak acid cation exchangers.

in organic or aqueous media, at a temperature of about 40–50°C, and reaction times of 6–8 h. It must also be mentioned that amination with the two amines, in contrast to the chloromethylation reaction, does not lead to crosslinking side reactions. When the reactions are carried out in water, a side reaction can occur at a very low level from the hydrolysis of a small number of $-CH_2Cl$ groups.

The chemical structures of strong base anion exchangers of Types I and II are not very stable in alkaline media because of the well-known Hofmann degradation, a property of quaternary ammonium compounds; the Type II displays a lower stability in alkaline media than Type I.

Hofmann degradation of the two structures takes place according to **Figure 6**. The degradation can lead to both loss of exchange capacity (routes A and A′ in Figure 6) and the appearance of a weak base capacity caused by the presence of tertiary amine groups (B, B′ and C in Figure 6).

Strong base anion exchangers have a lower thermal stability than the cation exchangers.

Other commercially available strong base exchangers are those formed with an acrylic matrix. They are usually made in bead form by free-radical polymerization of 3-dimethylaminopropyl methacrylamide with DVB followed by a quaternization reaction of the copolymer with alkyl halides as shown

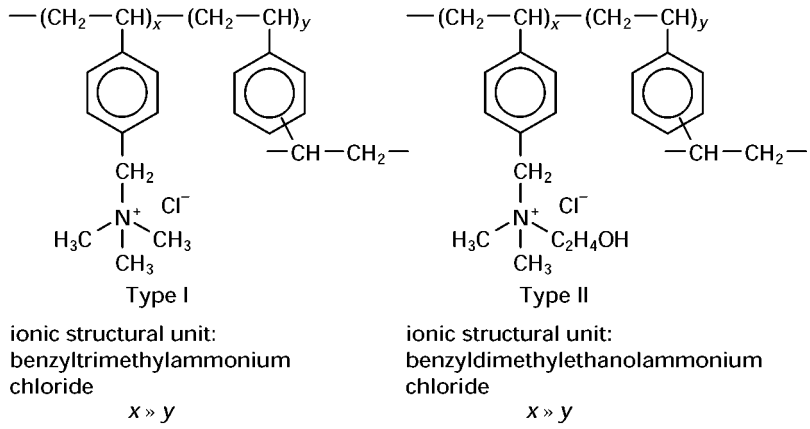

Figure 4 Classical structures of the structural units of Type I and Type II strong base anion exchangers.

in **Figure 7**. For the quaternization, gel- or macroporous-type copolymers can be used.

Generally, the acrylic strong base anion exchangers have a lower stability to hydrolysis, especially under acid or alkaline conditions, compared to the polystyrene-based exchangers. The hydrolysis becomes more significant when the spacer between the amide group and the quaternary group decreases in size. Thus, the product with a spacer of only one methylene group between the two functional groups has hydrolytic instability. The same phenomenon occurs in the anion exchanger prepared from 3-dimethylaminopropyl methacrylate, $CH_2{=}C(CH_3)COO(CH_2)_3N(CH_3)_2$, instead of the amide monomer.

In addition to the strong base anion exchangers previously presented as commercially available products, other specialized strong base exchangers are known.

In an effort to develop anion exchangers with preference for the NO_3^- anion over the SO_4^{2-} anion (an important factor for nitrate removal from potable water which invariably contains sulfate), the design of such a structure was conceived. It is the reaction product of the chloromethylated styrene–DVB copolymer with triethylamine, and can be described as a strong base anion exchanger of Type III.

Gel or macroporous 4-vinylpyridine–DVB copolymers are the precursors for strong base

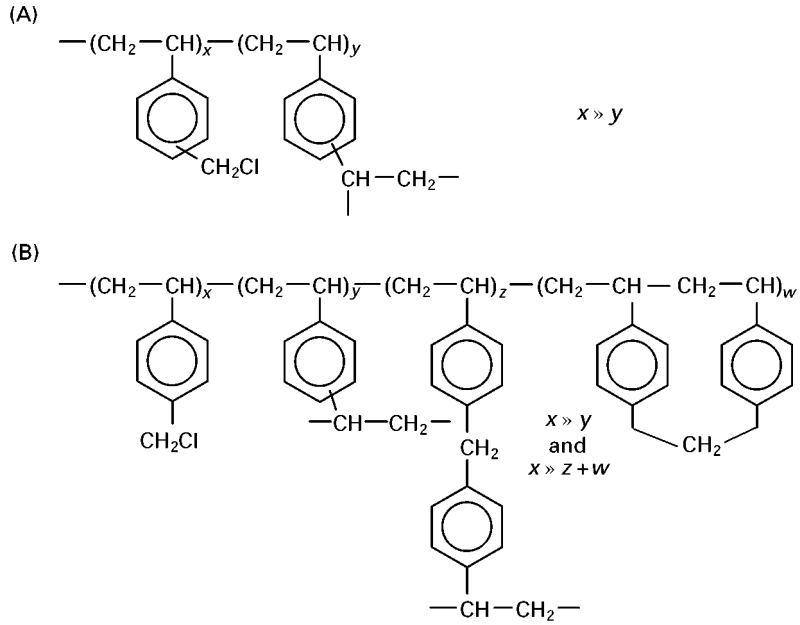

Figure 5 The two crosslinked polystyrene-based chloromethylated structures.

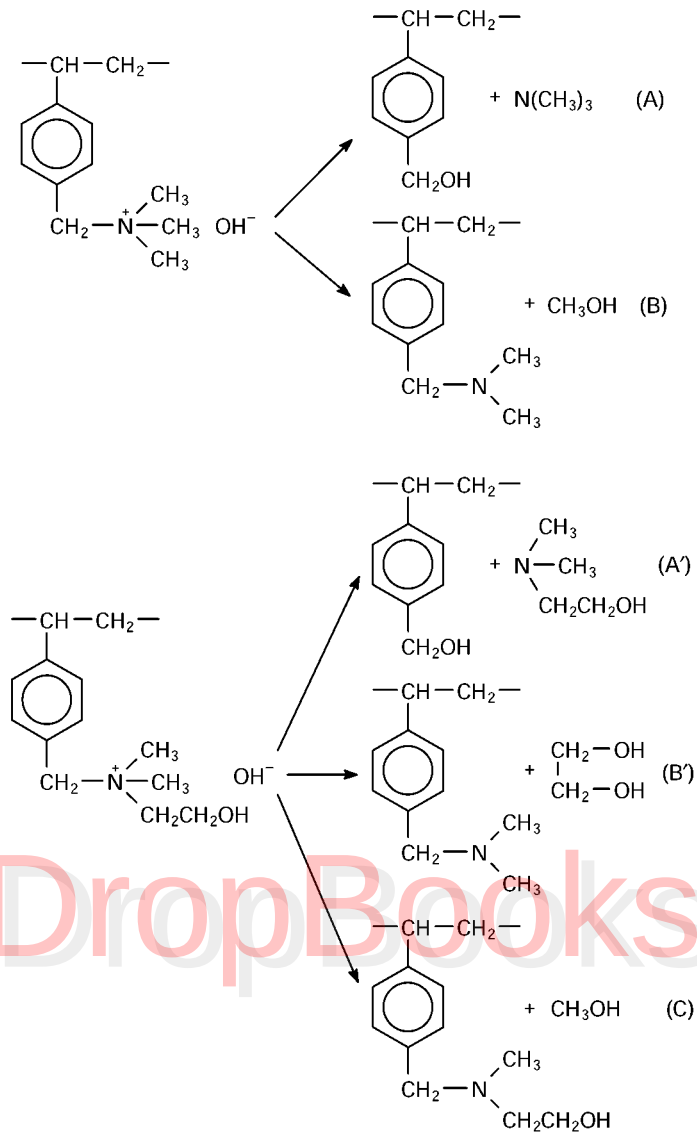

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Figure 6 Hofmann degradation of Type I and Type II strong base anion exchangers.

exchangers. These exchangers are made by the well-known quaternization reaction with alkyl halides as shown in **Figure 8**.

The synthesis of this category of anion exchangers takes place by a single chemical transformation step which avoids crosslinking side reactions. However, these exchangers cannot be utilized in many fields of application because of their very low chemical stability in alkaline media.

Ion exchangers with benzyltrialkylphosphonium groups, especially benzyltri-n-butylphosphonium halide can be made. These structures are not used in ion exchange processes but have special applications as phase-transfer catalysts. For the improvement of their properties, structures with a spacer larger than one methylene group between the aromatic ring and the phosphonium group have been synthesized. **Figure 9** shows the phosphonium-type structures and their preparative routes.

Commercially available exchangers of Types I and II are fully ionized in the whole pH domain of the aqueous medium, like the strong acid ones. The Type I exchanger is such a strong base that a considerable quantity of NaOH is required for its regeneration in the OH form, while the Type II exchanger, a weaker base, requires less. This aspect is an advantage of the Type II structure over Type I.

The strong base anion exchangers in their OH form react with both strong and weak acids. With the latter, the strong base anion exchanger of Type I is more effective than Type II. Because of this situation, Type I exchangers are used for soluble and

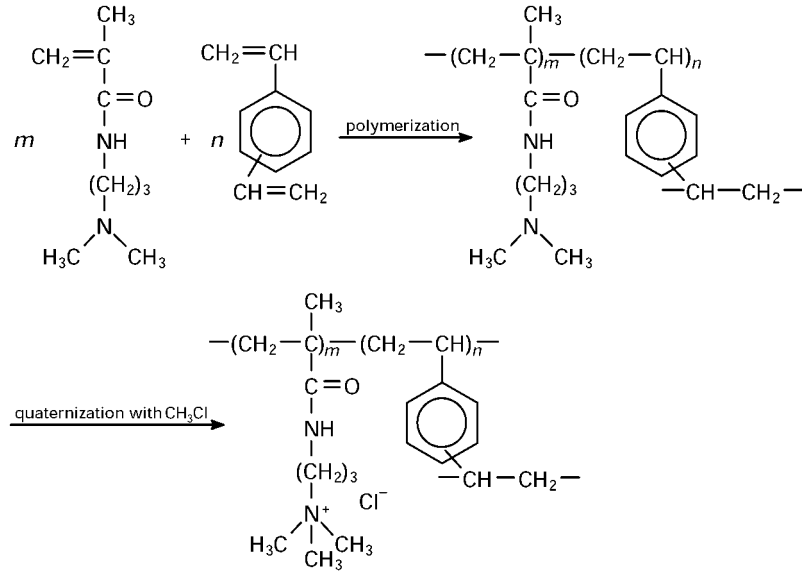

Figure 7 Preparation of an acrylic strong base anion exchanger.

colloidal silica removal from natural waters. For removal of the colloidal silica only, Type I strong base anion exchangers with special macroporous structures are effective.

Certain Type I strong base exchangers in their Cl form are used for adsorption of ionic organic compounds and are called 'scavenger' ion exchangers.

Weak Base Anion Exchangers

Commercial weak base anion exchangers are prepared by the condensation of *m*-phenylenediamine with formaldehyde. The chemical structure of this exchanger is illustrated in **Figure 10**. In this structure, the amine groups directly attached to benzene rings have a very low basicity.

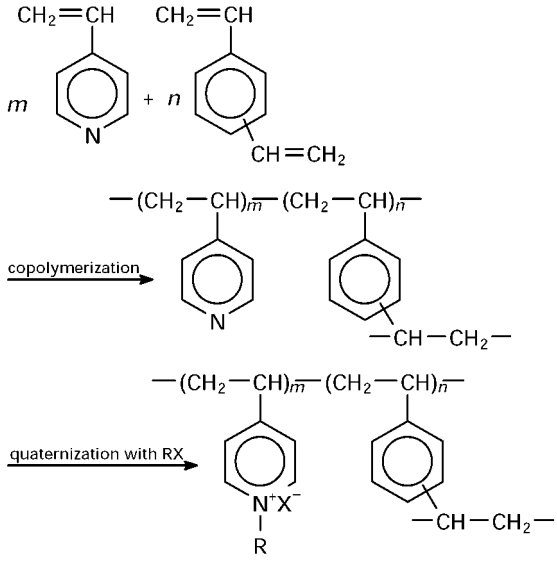

Figure 8 Preparation of strong base anion exchangers based on 4-vinylpyridine–DVB copolymer.

Polycondensation weak base exchangers with higher basicity were later obtained by the condensation of other reagents. An example is the epoxy structures formed by the condensation of aliphatic polyamines with epichlorohydrin. This halo-epoxy compound can react even with tertiary amine groups, thus anion exchangers containing amine and quaternary ammonium groups can be obtained as shown in **Figure 11**.

The most readily available commercial weak base exchangers are the polymerization structures based on polystyrene or acrylic matrices containing primary, secondary or tertiary amine groups, or all these groups together.

The polystyrene-based weak base exchangers are obtained by the same reaction scheme as the strong base ones with polystyrene matrices, but with the difference that dimethylamine is used in the amination step instead of trimethylamine or dimethylethanolamine. When using the secondary amine, in contrast with the tertiary amines, besides the main amination reaction which leads to the tertiary amine groups, an undesirable side reaction can also take place. This is the quaternization reaction between the pre-attached tertiary amine and $-CH_2Cl$ groups. It can take place intra- or inter-chain but both situations can occur.

The chemical structures of aminated units are shown in **Figure 12**. Both quaternization types (inter- and intra-chain) lead to anion exchangers with mixed

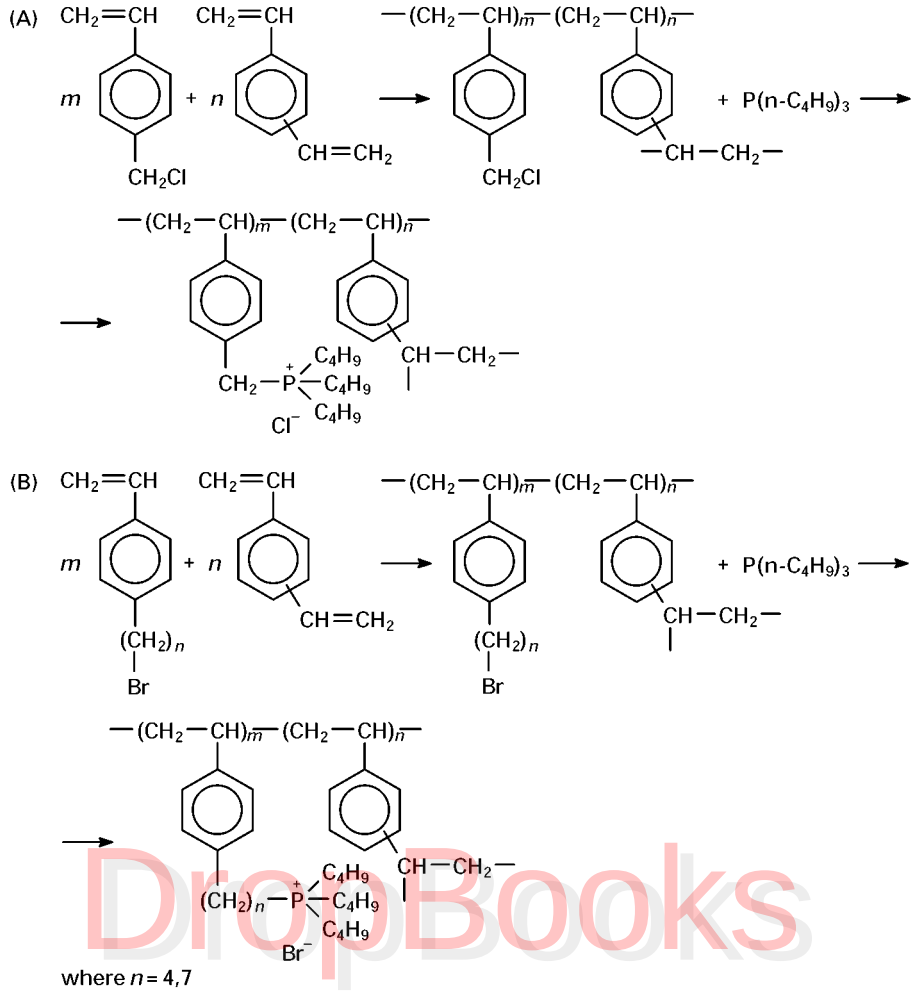

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Figure 9 Preparation methods of phosphonium-type strong base anion exchangers.

functional groups and the inter-chain ones also control the degree of crosslinking.

Amination takes place quantitatively under mild conditions (30–40°C; 4–6 h) in aqueous or organic media. By using a large excess of amine, the side quaternization reaction is greatly reduced.

The most common acrylic weak base exchangers are made by the acylation of primary or secondary amines. This reaction with esters, so-called ester aminolysis, is the most frequently used method to produce acrylic weak base exchangers.

The aminolysis of macroporous or gel-type ethyl acrylate–DVB copolymers, in bead form, with 3-dimethylamino-1-propylamine, ethylendiamine or other aliphatic polyamines, is illustrated in **Figure 13**.

The same structures can also arise from aminolysis–hydrolysis reactions of acrylonitrile–DVB copolymers. An example is shown in **Figure 14**.

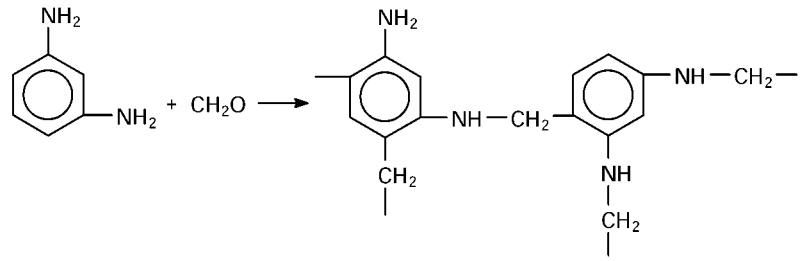

Figure 10 Chemical structure of *m*-phenylenediamine–formaldehyde weak base anion exchanger.

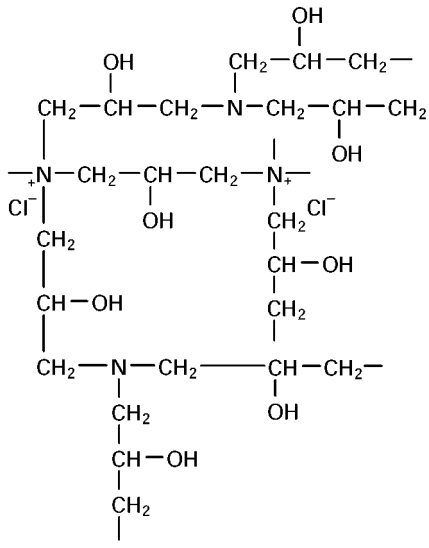

Figure 11 Chemical structure of an epoxy-type base anion exchanger.

The aminolysis and aminolysis–hydrolysis reactions take place under more stringent reaction conditions (temperature over 100°C and reaction time over 10 h) than the amination of the chloromethylated styrene–DVB copolymers.

Acrylic weak base exchangers synthesized from aliphatic polyamines have much higher exchange capacities than polystyrene-based structures.

The weak base exchangers cannot be regarded as typical ionic polymers since their amine groups are ionized only under certain conditions. Thus, an amine group in an alkaline medium is in the free-base form, but in a neutral medium it can exist in a partial ionization level, which depends upon amine basicity. In an acid medium a high level of ionization is present and because of this, the weak base exchangers are usually used to retain strong acids in water treatment. They also can be used as insoluble acceptors of acids in different chemical reactions such as the preparation of esters from acid chlorides and alcohols, etc. For the latter aim, the best known are the 4-vinylpyridine–DVB copolymers with a low degree of crosslinking.

Scheme 2 shows some more distinctive ion exchange reactions for the four above-mentioned types of exchangers.

Amphoteric Ion Exchangers

Ion exchangers which contain both acidic and basic groups are called amphoteric resins. Usually their matrix has some structural units with acidic groups and other units with basic groups.

Very interesting amphoteric resins are the so-called 'snake-cage polyelectrolytes'. One feature distinguishes the snake-cage polyelectrolytes from other amphoteric resins, namely the acidic and basic groups are not attached to the same matrix. For example, a snake-cage polyelectrolyte is prepared by polymerization of acrylic acid (snake) into a strong base anion exchanger with quaternary ammonium groups (cage). These resins are excellent reversible sorbents for electrolytes and can be regenerated by rinsing with water. Electrolyte sorption seems to be mainly determined by the preference of the acidic groups for the cation and of the basic groups for the anion. The resins show preference for different electrolytes. This phenomenon can be used for separating electrolytes one from another.

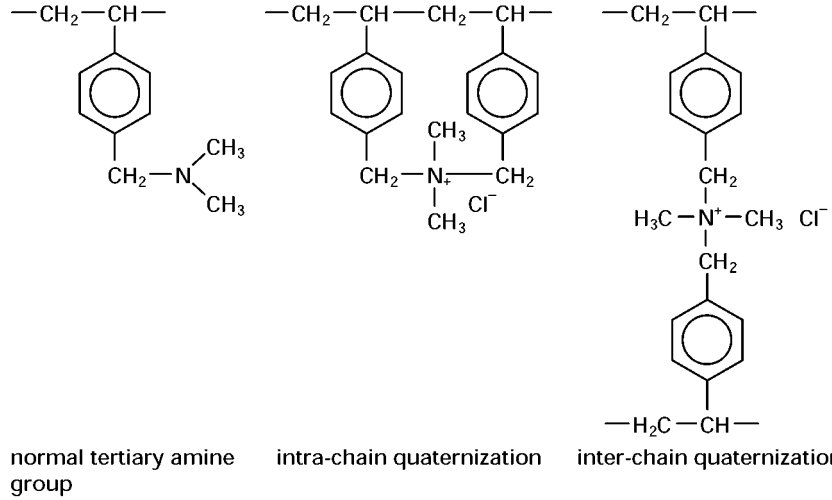

Figure 12 Chemical structure of the functional groups which can exist in a polystyrene-based weak base anion exchanger.

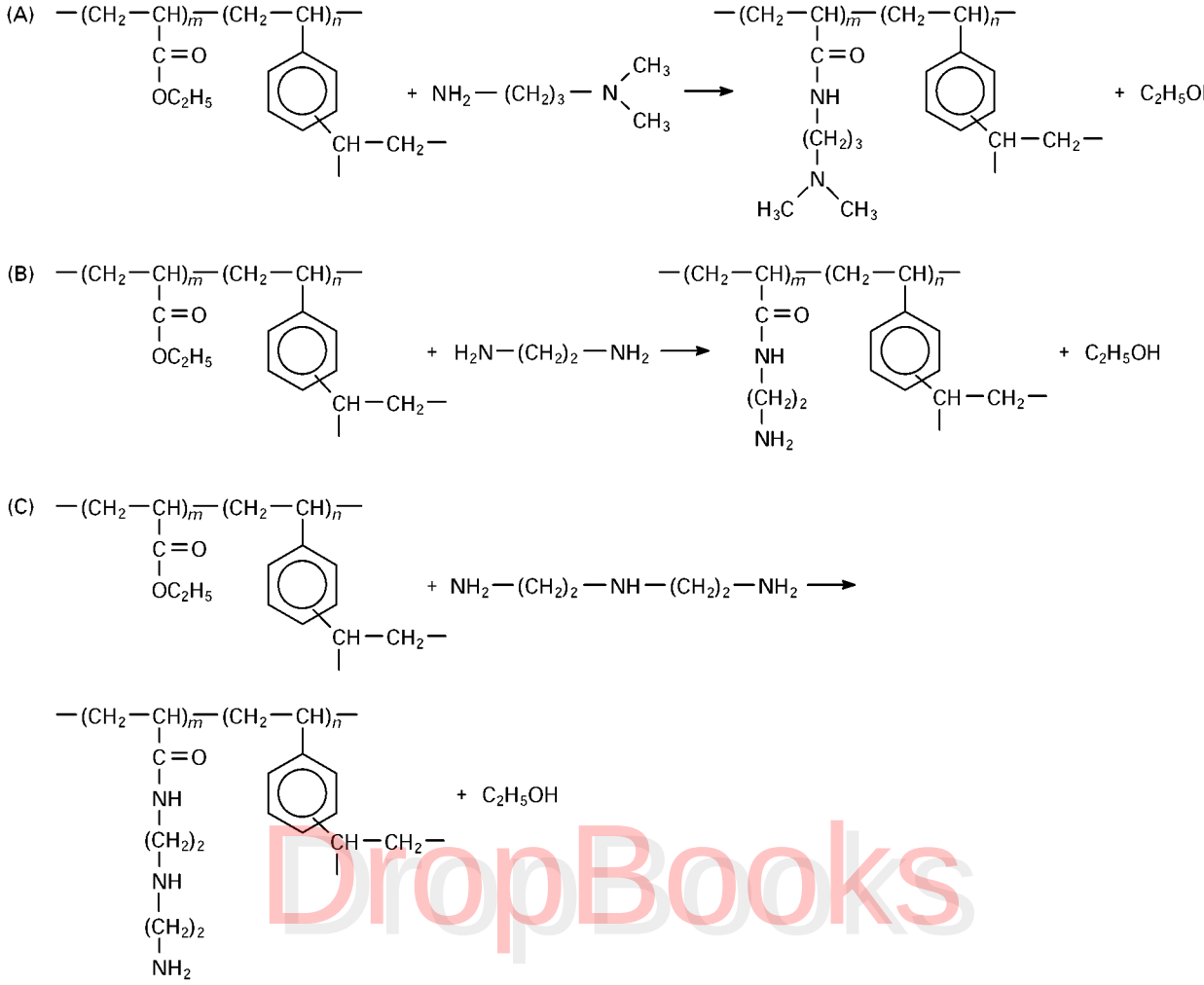

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Figure 13 Acrylic-type weak base anion exchangers and their preparation methods.

The snake-cage polyelectrolytes are also used in the technique of 'ion retardation'. This technique is the separation of strong electrolytes from weak electrolytes or non-electrolytes.

Chelating Ion Exchangers

The cation binding of transition, heavy and noble metals can be performed by an ion exchange process with strong and weak acid cation exchangers as well as with strong base exchangers; the latter are used if the metal cations are present in the form of complex anions.

However, the most promising technique for the binding of metal cations is the use of ion exchangers which contain chelating functional groups. Thus, exchangers with iminodiacetate groups can remove several ppm of Ca^{2+}, Mg^{2+} or Sr^{2+} from brine, in contrast to cation exchangers containing the

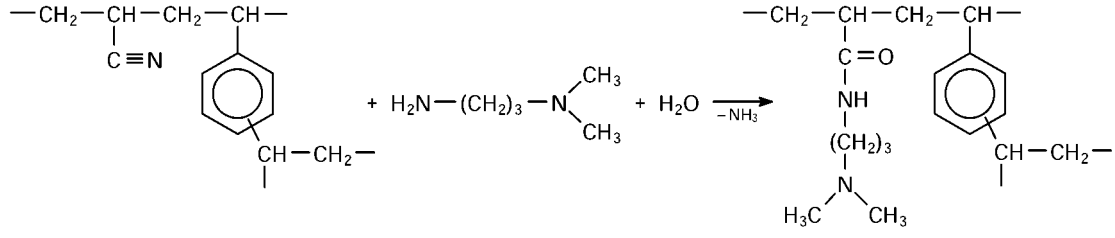

Figure 14 Preparation of an acrylic-type weak base anion exchanger from acrylonitrile–DVB copolymer.

Strong acid cation exchangers

$$2\,P{-}SO_3H + \begin{pmatrix}Ca\\Mg\end{pmatrix}Cl_2 \rightleftharpoons (P{-}SO_3)_2\begin{pmatrix}Ca\\Mg\end{pmatrix} + 2\,HCl$$

$$2\,P{-}SO_3H + \begin{pmatrix}Ca\\Mg\end{pmatrix}(HCO_3)_2 \longrightarrow (P{-}SO_3)_2\begin{pmatrix}Ca\\Mg\end{pmatrix} + H_2O + CO_2$$

$$P{-}SO_3H + NaCl \rightleftharpoons P{-}SO_3Na + HCl$$

$$P{-}SO_3H + NaHCO_3 \longrightarrow P{-}SO_3Na + H_2O + CO_2$$

$$P{-}SO_3H + NaOH \longrightarrow P{-}SO_3Na + H_2O$$

$$P{-}SO_3Na + HCl \rightleftharpoons P{-}SO_3H + NaCl$$

$$2\,P{-}SO_3Na + \begin{pmatrix}Ca\\Mg\end{pmatrix}Cl_2 \rightleftharpoons (P{-}SO_3)_2\begin{pmatrix}Ca\\Mg\end{pmatrix} + 2\,NaCl$$

Weak acid cation exchangers

$$P{-}COOH + NaHCO_3 \rightleftharpoons P{-}COONa + H_2O + CO_2$$

$$2\,P{-}COOH + \begin{pmatrix}Ca\\Mg\end{pmatrix}(HCO_3)_2 \longrightarrow (P{-}COO)_2\begin{pmatrix}Ca\\Mg\end{pmatrix} + H_2O + CO_2$$

$$P{-}COOH + NaOH \rightleftharpoons P{-}COONa + H_2O$$

$$2\,P{-}COONa + \begin{pmatrix}Ca\\Mg\end{pmatrix}Cl_2 \rightleftharpoons (P{-}COO)_2\begin{pmatrix}Ca\\Mg\end{pmatrix} + 2\,NaCl$$

Strong base anion exchangers

$$P{-}NR_3OH + HCl \longrightarrow P{-}NR_3Cl + H_2O$$

$$P{-}NR_3OH + H\begin{pmatrix}HSiO_3\\HCO_3\\HS\end{pmatrix} \rightleftharpoons P{-}NR_3\begin{pmatrix}HSiO_3\\HCO_3\\HS\end{pmatrix} + H_2O$$

$$P{-}NR_3OH + NaCl \rightleftharpoons P{-}NR_3Cl + NaOH$$

$$P{-}NR_3Cl + R_1COONa \rightleftharpoons P{-}NR_3OOCR_1 + NaCl$$

$$P{-}NR_3Cl + R_1SO_3Na \rightleftharpoons P{-}NR_3O_3SR_1 + NaCl$$

Weak base anion exchangers

$$P{-}NH_2 + H_2O \rightleftharpoons PNH_3OH$$

$$P{-}NH_2 + H_2O + NaCl \rightleftharpoons P{-}NH_3Cl + NaOH$$

$$P{-}NH_2 + H_2O + HCl \rightleftharpoons P{-}NH_3Cl + H_2O$$

(P is a polymer structure unit that contains an acid or base group.)

Scheme 2 Some distinctive ion exchange reactions.

Table 2 Some chelating acid and base functional groups

Functional group	*Chemical structure*	*Utilizations*
Amine	$-NH-(-C_2H_4-NH-)_x-H$	Removal of transitional metals
Iminodiacetic	$-N-(-CH_2-COOH)_2$	Selective removal of heavy metals
Isothiouronium	$-S-C(NH_2)=NH$	Selective removal of mercury and noble metals
Aminophosphonic	$-CH_2-NH-CH_2-P(O)(OH)_2$	Especially for decalcification of brine solutions
Phosphonic acid	$-P(O)(OH)_2$	Preconcentation of uranyl ions
Hydroxamic acid	$-CO-NHOH$	Selective retention for Fe(III) ions
Hydroxyamine	$-CH_2-N(CH_3)-CH_2-(CHOH)_4CH_2OH$	Selective retention for boric acid

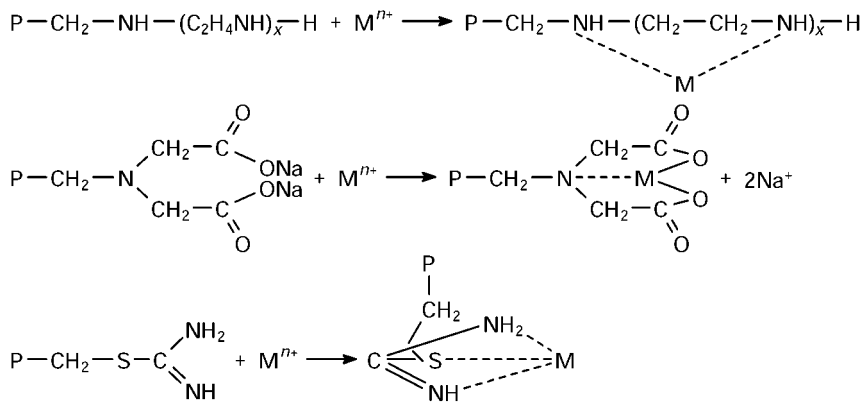

Figure 15 Classical binding of metal cations by some chelating functional groups. (P is a polymer structure unit that contains an acid or base group.)

non-chelating common acid groups. The latter exchangers show a higher selectivity for divalent cations than for Na^+, but the difference is not very large, so that they will not be able to bind Ca^{2+}, Mg^{2+} or Sr^{2+} cations present at very low concentrations.

The high selectivity of chelating ion exchangers is attributed to the establishment of much stronger bonds than the simple electrostatic attractive forces present in the case of the common ion exchangers. Because of these bonds, the chelating processes show a high degree of irreversibility.

It must be mentioned that the chelating groups, attached to polymer networks, are groups with two or more electron donor elements, such as N, S, O and P, and they can function like the model low molecular weight chelating agents. Their preparation takes place in two main ways – polymerization or polycondensation.

Table 2 shows some functional groups, which are capable of chelating. The binding of metal cations by some chelating functional groups is illustrated in **Figure 15**.

The nature of metal cation binding can be modified by changing the pH of the solution to cause chemical modification of the chelating groups. Thus, amine and isothiouronium groups can take part in the equilibria, shown in **Figure 16**. These groups will bind metal cations by a coordination process in neutral or base media via the free base forms while in an acid medium the same cations will be bound as complex anions by an anion exchange process via the salt forms.

Conclusions

The area of organic ion exchangers remains a very active one with intensive technical and scientific work on both conventional resins and entirely novel systems. Thus, organic ion exchangers with different morphologies of their three-dimensional networks and base and acid groups with various chemical structures have been prepared.

There is also a growing interest in the development of selective chelating ion exchangers for the possible application of these resins in analytical chemistry, metal recovery and wastewater treatment. The latter two applications have a great importance in economic and ecological domains. Requirements of the properties of these ion exchangers include high capacity, high selectivity and fast kinetics. Most of the

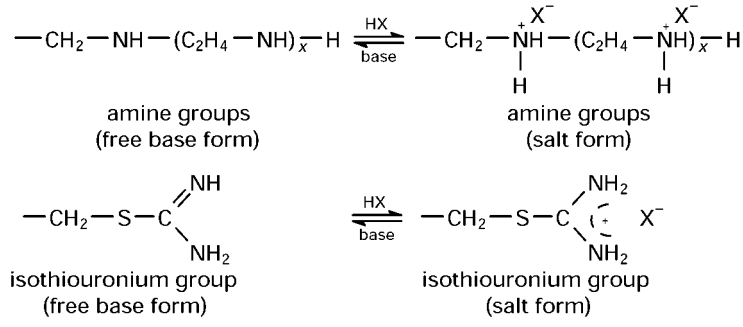

Figure 16 Chemical structure dependence of amine and isothiouronium groups on the pH of aqueous medium.

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commercial resins show a high capacity but a poor selectivity towards metal ions.

The combination of the physical strength of an inorganic support with the higher ion exchange capacity and kinetics of the organic ion exchangers could, in the future, lead to an interesting class of ion exchangers with special applications.

See also: **II/Ion Exchange:** Historical Development; Inorganic Ion Exchangers; Organic Membranes; Theory of Ion Exchange.

Further Reading

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Organic Membranes

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Organic ion exchange membranes are made of insoluble polymeric foils, tubes or hollow fibres to which ion exchange groups are covalently bound. The membranes have all the properties typical of ion exchange resins and the ability to keep two different solutions physically separated. Thus, the main property of an ion exchange membrane is a selective exchange of ions and a selective permeability to ions, water or other specifically membrane-soluble species. Although optimizing all the properties would be difficult in the case of one membrane used for a variety of applications, the most desired property is always high membrane selectivity, which allows the separation of ions with low energy consumption and high transport rates. There are many additional requirements for ion exchange membranes, such as low electric resistance, high permselectivity, low free diffusion of salts (leakage), low osmotic water transport, high mechanical strength, high selectivity between ions of the same charge and high chemical stability.

Preparation

Ion exchange membranes can be classified as monopolar or bipolar. In parallel, some intermediate membranes have been categorized as mosaic and amphoteric. The monopolar membranes can be divided into cation exchange membranes and anion exchange membranes. Combination of these membranes results in a bipolar ion exchange membrane.

The properties of any ion exchange membrane are determined by the properties of its polymer matrix and the type and concentration of the fixed ionic moieties. The polymer matrix of ion exchange membranes is usually cross-linked. The degree of cross-linking extensively influences the degree of swelling (water sorption), chemical and mechanical stability and membrane permeability by changing ionic mobility inside the membrane phase. Thus, the proper selection of membrane components, their content and the method of preparation significantly affect the membrane properties and structure. The subsequent chemical modification of the polymer matrix involves the introduction of ionogenic groups, resulting typically in the following fixed sites:

Cation exchange membranes:

$$-SO_3^-, -COO^-, -PO_3^{2-}, -HPO_2^-, SeO_3^-$$

Anion exchange membranes:

$$-NH_3^+, -RNH_2^+, -R_3N^+, =R_2N^+, -R_3P^+, -R_2S^+$$